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During the period stated, I participated with V. Oberbeck in a study to explore the effectiveness of comets for chemical evolution. Although many organic compounds must have been required to originate life, I performed a mathematical analysis of the concentration of amino acids in various terrestrial environments because there is evidence that amino acids formed as a result of cometary impact. As suggested by Dr. Oberbeck, I first estimated the initial concentration of amino acids in surface environment after cometary impact because this was critical to the process of evolution. Because amino acids in the ocean after cometary impact depended on their sinks, I considered the effect of hydrothermal vents, ultraviolet rays and clays.

I considered the net concentration of amino acids in pure sea water from corona discharge and ultraviolet sinks and compared it with concentration from cometary impact. Next, I analyzed the absorption of amino acids by clay particles before degradation by ultraviolet light and finally compared the effectiveness of clays, ultraviolet and hydrothermal vents as sinks for cometary amino acids.

The research done is completely detailed and included in a preprint of a paper: "Chemical Evolution of Cometary Amino Acids on Bombarded Earth" submitted to **Origins of Life and Evolution of the Biosphere**. A preprint of this paper is enclosed to make this report complete.

Chemical Evolution of Cometary Amino Acids on The Bombarded Earth

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Abstract

It is proposed that the AIB amino acids at the K/T boundary were synthesized during entry of a comet. However, whether they were synthesized or supplied directly from space, the concentration of amino acids in the shallow K/T sea would have been about 10^{-7} M. It is probable that clays were the dominant sinks for the amino acids in the K/T sea and in the primordial ocean. Because clay removed amino acids from sea water quickly, we must study the amino acid contribution from individual comets in order to evaluate the effectiveness of comets for chemical evolution. Such an evaluation shows that comets would have produced amino acid concentration higher than equilibrium concentrations of amino acid from corona discharge at all times preceding the age of the oldest fossils. The preferred sites for chemical evolution of cometary amino acids are in cloud drops and tide pools where the concentration of amino acids would have been the highest. Life could have originated at the surface even during periods of intense bombardment of the earth before 3.8 billion years ago.

Introduction

In this study, we explore the effectiveness of comets for chemical evolution. The possibility that comets have an important role in chemical evolution was pointed out by Oro (1961) and more recently considered by Clark (1988), Oberbeck et al (1988), and Chyba et al. (1990). Although many organic compounds must have been required to originate life, we focus on amino acids because there is evidence that they formed as a result of cometary impact. We first estimate the initial concentration of amino acids in surface environments after cometary impacts because this was critical to the process of chemical evolution. For example, Stribling and Miller (1987) noted that a 10^{-4} molar concentration of amino acids in the primordial oceans would have been sufficient for

chemical evolution, but lower concentrations would not have been of much use. In addition, the laboratory experiments of Lahav et al. (1978) also show that high concentrations of amino acids were required for peptide formation.

Because amino acid concentration in the ocean after cometary impact depended on their sinks, we must consider a variety of potential terrestrial sinks. Therefore, we consider the effects of hydrothermal vents, ultraviolet light, and clays. It is concluded that clays or other minerals were the probable dominant sinks for cometary amino acids in the primordial ocean. Amino acids supplied from comets could have been absorbed from sea water quickly by clay where they would have been protected from ultraviolet light but they could have been destroyed by ultraviolet light in pure sea water in less than 100 years. Rapid absorption of amino acids by clay or destruction by ultraviolet light means that we must examine the fate of amino acids resulting from individual cometary impacts

The Initial Concentration of Amino Acids in Sea Water After Impact of a 10 Km Comet.

The surface density of AIB amino acid in the K/T sediments at Stevns Klint Denmark is $5 \times 10^{-5} \text{ gms/cm}^2 = 4.85 \times 10^{-7} \text{ moles/cm}^2$ (Zhao and Bada, 1989). The amino acids in the K/T sediments could have been synthesized after cooling of the vapor cloud formed from the heat of impact of a comet at the surface. Barak and Bar-Nun (1975) performed shock tube experiments in which simple hydrocarbons, ammonia, and water vapor, were subjected to shock temperatures that exceeded 2000°K . Much higher temperature than 2000°K exist in a fireball produced by cometary impact. However, we believe that the results of Barak and Bar-Nun (1975) are very useful guides to the amounts of amino acids that could have been synthesized during cometary impact. The sample temperature in the shock tube experiments were sufficient to break the chemical bonds in the ammonia, water vapor, and hydrocarbons and form the radicals that produced compounds that formed the amino acids. Therefore, amino acid precursors could have been synthesized during cometary entry as the excited radicals, produced at much higher temperatures than those reached during the Barak and Bar-Nun experiments, recombined during cooling of the vapor cloud at the recombination temperature below the peak dissociation temperatures reached in the Barack and Bar-Nun experiments.

Moreover, not all of the products would have been oxidized carbon. Mukhin et al. (1987) vaporized ordinary chondritic meteorite samples and produced a variety of compounds including CO₂ as well as reduced carbon compounds including formaldehyde and HCN. This demonstrates that carbon compounds of various oxidation states, including amino acid precursors, can be produced as products of the same vaporization experiment. Would amino acids have been produced from impact vaporization of an object with as much oxygen as is found in a comet?

Examples were selected from the Barak and Bar-Nun (1975) experiments so as to provide a range of O/C for shock tube reactants that encompass the range in uncertainty of O/C for comets. The total yield of all amino acids produced in these shock tube experiments was calculated in terms of the mass of CHON for the reactants for these experiments and yields were accumulated in bar charts on the Y axis in figure one. Although the relative amounts of different amino acids change with O/C ratio, there is no apparent correlation of total amino acid yield with ratio of O/C. Note that the total range in O/C for the selected experiments span the range of uncertainty of the O/C ratio in Comet Halley. This range of uncertainty for comets, shown at the bottom of the figure beneath the X axis, was calculated from the values and uncertainties in composition of carbon and oxygen given for comet Halley in Delsemme (1989). There were two shock tube series of experiments for which Barak and Bar-Nun believed that AIB amino acid was produced. They are the experiments with O/C ratios of 1.4 and 1.0. The experiment where the O/C ratio was 1.4 was the one in which the ratios of O/H and O/N was also nearest to that for comets. This shock tube experiment produced 1.4×10^{-5} moles total all types of amino acids per gm CHON reactant.

The minimum mass of the K/T impactor was, according to O'Keefe and Ahrens, (1982) equal to 4×10^{17} gm. We calculated the mass fraction of CHON in comets from the mass fractions for elements C, H, O, and N in comets given in Delsemme (1989) and found it to be 0.86. Thus, the minimum mass of CHON in the K/T comet is 3.5×10^{17} GMS. From this and the production rate for all types of amino acids by shock synthesis as given above, we predict that the total minimum amino acid concentration of all types of amino acids in a 100 meter deep inland sea at the Stevns Klint locality should have been $(3.5 \times 10^{17})_{\text{GMS HCON}} (1.4 \times 10^{-5}) \text{ moles/gm CHON} / (5 \times 10^{18} \text{ cm}^2) \text{ EARTH SURF AREA} (10 \text{ L/cm}^2) = 1 \times 10^{-7} \text{ MOLES/L}$. The minimum column density of AIB alone expected at the K/T site is obtained by multiplication of the average yield of AIB in the two shock tube experiments (.87 micromoles per gram HCON) by the minimum mass of

HCON above. We obtain a minimum predicted column density of 6.3×10^{-6} gms/ cm² which is less than an order of magnitude less than the observed value of 5.0×10^{-5} gms/ cm².

Zahnle and Grinspoon (1990) argue that the K/T amino acids are those that arrived in dust that separated from the comet in space and arrived before and after the comet nucleus. However, there are several difficulties with this view as already discussed by the authors. Perhaps the greatest difficulty is that the ratio of AIB and iridium is much higher than that observed in carbonaceous meteorites.

A remaining possibility for origin of the K/T AIB is that the K/T amino acids survived cometary entry and impact. Chyba et al (1990) concluded that trace amounts of organic compounds such as amino acids could have survived only in a very restricted size range of 50-200 meter diameter comets. Organic compounds in larger comets were pyrolyzed. The Chyba et al. (1990) calculations of comet impact velocity relies on the comet remaining coherent and unfragmented so that organics are preserved during passage through the atmosphere and so that its deceleration may be computed accurately. They do not consider the physics of fragmentation during entry because they feel the process is poorly understood. However, they state that their estimates of the amount of organics surviving impact are conservative if fragmentation occurred because the increased surface area resulting from fragmentation during entry would lead to even more deceleration, lower impact velocities, and more material surviving lower impact shock heating. However, we doubt that amino acids survived during atmospheric entry even in small comets because the increased surface area could have lead to increased vaporization of the comet during entry through the atmosphere. For example, the results of Bronshten (1983) indicate that fragmentation is followed by increase in the surface area which leads to acceleration of vaporization during entry of small icy objects. Additional work suggests that organic material in small comets may not survive entry. Equation 14 of O'Keete and Ahrens (1982) indicates to us that penetration time can exceed ablation time for entry of 50-200 meter diameter comets in a probable ten bar early atmosphere.

There is another reason that suggest that the K/T cometary amino acids, if present in the comet, did not survive impact. If the K/T comet contained 12 ppm of amino acids as for carbonaceous chondrites (Cronin, 1983), there would not have been sufficient amino acids in the 4×10^{17} gm comet to produce the observed column density at Stevns Clint Denmark. For example, it may be shown using the 12 ppm for

amino acid concentration in the carbonaceous chondrites such as Murchison, the total column density of AIB in the K/T sediments would have been only 1.6×10^{-7} gms/ cm² even if all of the material survived impact.

However, what would the concentration of all types of amino acids have been in the K/T seas if the amino acid content in the comet was originally in the comet and if all of it did, in fact, survive impact. Let us assume that the ratio of total amino acids of all types to AIB for the impactor is similar to that observed in carbonaceous meteoroids, the only objects from space that are known to contain amino acids. The ratio of all types of amino acids and AIB in hot water extracts of Murchison carbonaceous chondrite is about 5 according to Cronin (1976a). Cronin (1976b) suggests that amino acid precursors also exist in the meteorite and that they form amino acids during subsequent hydrolysis. This suggests that amino acid precursors could also form amino acids after deposition of precursors in the oceans. The ratio of all amino acids to AIB for both water extracts and samples exposed to acid hydrolysis was about seven. Therefore, we adopt a ratio of six for the ratio of total expected amino acids of all sorts to AIB for amino acids arriving from space.

The surface density of AIB amino acid in the K/T sediments at Stevns Klint Denmark is 5×10^{-5} gms/cm² = 4.85×10^{-7} moles/cm² (Zhao and Bada, 1989). Thus, the inferred column density of all amino acids with all the appropriate molecular weights in the sediments at Stevns Klint Denmark is 2.9×10^{-6} moles/cm². This is obtained from the inferred total amino acid column density which would have been equal to six times the column density of AIB in the sediments. Now, the maximum depth of the inland sea at Stevns Klint Denmark at the end to the Cretaceous period was, at most, 100 meters (Alvarez, 1980). Therefore, the amino acid concentration in a 100 meter deep inland sea would have been $2.9 \times 10^{-6}/10L$ or 2.9×10^{-7} moles/liter if the amino acids were those which existed in space and if the concentration in the impactor was very much greater than that that exist in carbonaceous chondrites and if all of it survived impact. Although we believe the amino acids could not have been those which survived impact, the key point for purposes of evaluating comets as agents for chemical evolution is that, whether the observed amino acids at Stevns Klint, Denmark survived impact or were synthesized, we can be relatively sure that the concentration of all amino acids in the shallow sea following the K/T impact was about 1×10^{-7} MOLES/ L.

Net Concentration of amino acid in Pure sea water after cometary impact and degradation by Ultraviolet light.

Because the concentration of organic compounds is important for chemical evolution and because the concentration depends on the sinks as well as the sources, it is important to determine how sinks changed the concentration of cometary amino acids with time. An early objection to chemical evolution was raised by Hull (1960) who argued that ultraviolet light would have efficiently destroyed amino acids and resulted in at most a 10^{-12} molar solution in sea water, thus defeating prospects for evolution of organic compounds on the early Earth. Of course, mechanisms for shielding and concentrating reactants from the degrading effects of ultraviolet light, including absorption by clay particles, were quickly proposed (Bernal, 1960). Nevertheless, amino acids, in pure sea water of the shallow seas, would have been degraded by ultraviolet light. Dose (1975) considered the effect of ultraviolet light on the degradation of amino acids in shallow primordial seas and found ultraviolet light to be a very effective sink for amino acids. He provided a relationship that can be used to calculate the concentration of amino acids $C(t)$ at any given time in terms of the initial concentration C_0 :

$$C(t) = C_0 e^{-\phi I \sigma t} \quad (1)$$

where ϕ , quantum yield for destruction is 10^{-2} , I , irradiation flux intensity $< 3000 \text{ \AA}$ is 10^{22} quanta/cm².yr, σ , absorption cross-section, is $6 \times 10^{-22} \text{ cm}^2/\text{molecule}$ and t is time in years. This simplifies to:

$$C(t) = C_0 e^{-0.6t} \quad (2)$$

We used equation (2) to calculate the change in concentration of amino acids in the shallow sea after the K/T cometary impact if the sea water was pure and if ultraviolet light was the sink for the amino acids supplied by the K/T impact. The initial concentration, C_0 , was taken as $1 \times 10^{-7} \text{ Moles/Liter}$ which was calculated in the last section. Results are shown in Figure one. Note that the concentration would have

changed very rapidly after the impact. Only one tenth of the initial concentration of amino acids produced in pure water of a shallow sea remained after 38 years. It is useful for the evaluation of the role of comets in chemical evolution to compare the changing amount of amino acids in pure sea water after an initial contribution by cometary entry with the equilibrium concentration of total amino acids that would have been present in pure sea water from classical sources such as corona discharge.

Net concentration of Amino Acids in Pure Sea Water From Corona Discharge and Ultraviolet Sinks, and Comparison with Concentration from Cometary Impact.

We now use the production rate for amino acids from corona discharge in the primordial atmosphere to estimate the equilibrium concentration of amino acids in pure sea water after production and degradation by ultraviolet light. In this event, there is a constant production of amino acids instead of only an initial contribution as is the case after a comet impact. Therefore, it is necessary to derive a new expression for the changing concentration of amino acids in the sea. The concentration of amino acids in the ocean after an elapsed time Δt is the net result of the amount present at the beginning, the amount produced in that time interval, and the amount destroyed by ultraviolet light. It is given by:

$$C(t + \Delta t) = k \Delta t + C(t) e^{-\phi I \sigma \Delta t} \quad (3)$$

Expressed as a differential equation, this becomes:

$$dC/dt = k - C(t) \phi I \sigma \quad (4)$$

The solution of this equation is:

$$\begin{aligned} C(t) &= k / \phi I \sigma [1 - e^{-\phi I \sigma t}] \\ &= k / \phi I \sigma [1 - e^{-0.06 t}] \end{aligned} \quad (5)$$

Note that as t approaches infinity in equation (5), the equilibrium value of $C(t)$

approaches 16.6 times the value of the production rate of amino acids, k , by corona discharge.

From Stribling and Miller (1987), we have an average amino acid production rate from corona discharge, k , in a CO_2 atmosphere, of 3.12×10^{-10} moles / cm^2yr . For deposition in a 100 meter inland sea, we use 10 liters of water per cm^2 of surface area to convert these production values to 3.12×10^{-11} moles /liter.yr. Substitution of this value into equation (4) and evaluation as a function of t gives the curve plotted in figure three. It may be seen that the equilibrium value is 5.18×10^{-10} moles per liter. The energy available from corona discharge might be appreciably less than used by Stribling and Miller (1987) as noted by Chyba and Sagan (1991). The calculation has been repeated using an energy values which is 30 times less than used by Stribling and Miller (1987) as suggested by the upper limit of the range in energy flux estimate for electric discharge suggested by Chyba and Sagan (1991). This gives a value of 1×10^{-12} moles/liter.yr for amino acid production by corona discharge in a CO_2 atmosphere. Repeating the calculation for concentration in the sea as a function of time we obtain the second curve shown in figure three. The equilibrium value of amino acid concentration is now 1.7×10^{-11} moles/liter.

Results given in figures two and three show that for about 90 years after the impact of a 10 km diameter comet (K/T comet), the concentration of amino acids that would have occurred in pure water of a shallow sea at Stevns Klint would have exceeded the maximum equilibrium concentration of amino acids in pure sea water that could ever have existed as a result of corona discharge in a predominantly CO_2 atmosphere, if the yields from Stribling and Miller are adopted. If the energy yield for electric discharges in the primitive Earth given in Chyba and Sagan (1991) and amino acid production obtained from Stribling and Miller (1987) are used, then the concentration following cometary entry would have exceeded the maximum equilibrium concentration from corona discharge for 150 years. Therefore, if the sea contained no clays or other sinks, the amino acids from comets would have produced higher concentrations of amino acids in pure sea water than corona discharge.

Absorption of Amino acids in Clay particles Before Degradation Ultraviolet Light.

We believe that there is evidence that clay was present in the K/T sea and it absorbed amino acids that formed as a result of cometary impact before their

concentration could have been decreased substantially by ultraviolet light. Zhao and Bada (1989) treated the K/T sediments including carbonates and clays with 6 M HCL and recovered the amino acids from the treated insoluble residue of smectite clay, smectite-illite and trace amounts of quartz. We believe that the amino acids could have been adsorbed on the smectite clay residue because of the following considerations. Lahav and Chang (1976) derived experimental relationships between amino acid absorption coefficients and smectite clay surface area per molecule of amino acids on smectite clay that was in equilibrium with amino acid-sea water solutions. There was about three grams of insoluble residue consisting of smectite, smectite illite with high percentages of expandable lattice, and trace quartz (Alvarez, 1980) in the two meters of a one cm² section of sediments from which the amino acids were recovered. The surface area of smectite clays is about 600 m²/gm. If the 5×10^{-5} gms/cm² of AIB in the K/T sediments were absorbed on smectite clay, the surface area of clay per molecule of AIB amino is 5.96×10^8 A²/ molecule AIB. The log of the surface area (A²) / molecule would be equal to 8.77. How does this value compare to the value predicted from the inferred initial concentration of amino acids in sea water after the K/T impact and the smectite clay-amino acid coefficient relationships presented by Lahav and Chang (1976).

The surface density of AIB was according to Zhao and Bada (1989) 5×10^{-5} gms/ cm². Alvarez (1980) give a maximum depth of the K/T sea as 100 meters but since this a maximum value we assume a possible range of depths between 10 m and 100m. This results in a range of uncertainty in AIB concentration in the sea water of 5×10^{-8} to 5×10^{-7} moles/ Liter. We have no absorption coefficient for AIB on smectite Clay but values for other amino acids of very similar composition are available. The absorption coefficient for AIB should be between that for alanine (Log k = -2.7 and Leucine (log k = -3.3 according to S. Chang, Pers. Comm., 1991). Therefore the predicted log of the surface area of clay per molecule of AIB on smectite clay is in the cross hatched area defining the uncertainty in the concentration of amino acids in the K/T sea and the absorption coefficients in figure four. The log of the surface area of clay per molecule of AIB in the K/T sediments (8.77) lies within the cross hatched range of uncertainties in the values of these parameters.

Therefore, the amino acids in solution in sea water after the K/T impact could have been in equilibrium with amino acids absorbed on smectite clay when the amino acid concentration was near the initial concentration immediately after impact. The

implication is that AIB was absorbed by clay and that ultraviolet light must not have acted as an effective sink for these amino acids because, in that event, the concentration would have been lower than the initial concentration and the predicted surface density of clay per molecule of amino acid would have then been lower than the observed values. In the event that the K/T amino acids were absorbed on carbonates rather than clays, the agreement of the predicted amino acid clay surface densities and observed densities would be highly circumstantial.

Note that the surface density of amino acids on clays after electric discharge and deposition in the sea would have been much less than that produced from impacts on the scale of the K/T impact. For example, even if we use the equilibrium concentration of amino acids from figure three for electric discharge and consult figure four, we find that the surface density of electric discharge amino acids would have been orders of magnitude less than those that were produced from the K/T comet impact which were then absorbed on clay particles.

Comparison of the effectiveness of clays, ultraviolet light and hydrothermal vents as sinks for cometary amino acids.

It has been suggested by Stribling and Miller (1987) that submarine hydrothermal vents acted as sinks for amino acids in the primordial ocean. According to Stribling and Miller (1987), amino acids from electric discharge were added continuously to a well mixed ocean, amino acids in water passing through the vents were destroyed, and water from the vents, free of amino acids, remixed with sea water that contained amino acids. According to this view, the ocean at any given time contained amino acids in solution in a well mixed condition, since the ocean water mixing time was short (one thousand years) compared to the time required to run an ocean volume of water through the vents (ten million years). Sea water, devoid of amino acids, from the vents was being added back into the well mixed ocean at a rate of $F = 1.5 \times 10^{14}$ liters per years. Amino acids from corona discharge were also being added to the ocean at a constant rate, k . Shock (1990) suggested that amino acids could have been metastable in vents and more recently he suggested that useful prebiotic reactants may have been the products of processing of cometary reactants by hydrothermal vents (Shock, 1991). We recognize the merit of these arguments, but we

now evaluate vents as if they were sinks for amino acids because Stribling and Miller (1987) suggested that hydrothermal vents were the *dominant* sinks for amino acids in the ocean.

We find, after expressing the model of Stribling and Miller (1987) mathematically that, after passage of an incremental time, Δt , from time t , the concentration of amino acids in the well mixed ocean is given by:

$$C(t + \Delta t) = C(T) + k \cdot \Delta t - (F/V) \cdot C(t) \Delta t. \quad (6)$$

where $C(t)$ is concentration of amino acids at time T , F is the flow rate through the vents, and V is ocean volume. After rearrangement and expression as a differential equation

we obtain:

$$dC(t)/dt + (F/V) C(t) = k \quad (7)$$

Integration of equation (7) gives:

$$C(t) = C_o e^{-Ft/V} + K(V/F) \{1 - e^{-Ft/V}\} \quad (8)$$

The volume V of the ocean is 1.5×10^{21} liters and the flow rate through the vents, F , is estimated by Edmond (1982), as 1.5×10^{14} liters per yr. We used equation (8) with $K=0$ to compute the time it would take for hydrothermal vents to reduce an initial concentration of amino acids from sea water, if passage through the vents destroyed amino acids. If it is assumed that vents destroyed amino acids, the initial concentration of amino acids in the ocean would have been reduced to 10% of the initial value after one million years.

How does a potential hydrothermal vent sink compare to the previously discussed ultraviolet and clay particle sinks? Equation (1) which gives the rate of degradation of amino acids of initial concentration C_o by ultraviolet light shows that the initial concentration of amino acids placed in the sea would be reduced to 10 % of its initial value in 38 years, a much shorter time than the ten million years it would have taken for vents to reduce an initial concentration of amino acids to the same level. We recall from the discussion above, that AIB amino acid was absorbed from solution at its

initial high concentration, in equilibrium with clay before any decrease in the initial concentration of amino acids by ultraviolet light. Therefore, it appears that clays were the dominant sinks for cometary amino acids that were supplied to oceans or inland seas at Stevns Klint, Denmark and in the primordial oceans as well.

Chemical Evolution of Cometary Reactants at the Surface of the Bombardment Earth.

We must next consider the probable sites for chemical evolution of cometary amino acids. This is required because impacts of asteroids or comets much larger than 10 km diameter were able to periodically sterilize the Earth's surface and interfere with chemical evolution. The degree to which giant impacts could have interfered with chemical evolution depends upon the site of chemical evolution. Higher energy impacts that were able to frustrate chemical evolution deep in the ocean occurred at lower frequency than lower energy impacts that would have been able to disrupt chemical evolution only at the ocean's surface (Maher and Stevenson, 1988, Oberbeck and Fogleman 1989a,b; 1990, Sleep et al, 1989). Therefore, we must evaluate probable sites for chemical evolution of amino acids from small comets within the context of these more energetic sterilizing asteroid and comet impacts.

According to Chang (1988), the nature of planetary environments that would have been favorable for chemical evolution are those existing at interfaces between different states of matter. Chang (1988) points out that evolved chemical systems and living systems represent a subset of highly organizing structures that are far from equilibrium with their environment. Chang hypothesized that they are sustained in places where large amounts of matter and energy pass; the environments typically have large gradients in physical parameters. Lahav et al. (1978) suggested that chemical evolution was enhanced in tidal lagoons, a major interface between air, land, and water. Lerman, (1986) suggested that bubbles at sea-air interfaces would have been ideal sites. Oberbeck et al. (1990) proposed that chemical evolution would have been accelerated in cloud drops. Corliss et al. (1981), Wachtershauser (1990), Shock (1990,1991) have stressed that prebiotic chemistry could also have occurred at hydrothermal vents where large amounts of energy and mass pass through submarine vents.

As we have shown, comets would have supplied important prebiotic reactants to Earth. Amino acids from comets would have been present first at interfaces between

cloud drops and air in cloud drops, then at the interface between the air and the water of the oceans., and finally at the hydrothermal vents. M. Mitchell Waldrop (1990) reported that the asteroid impact studies of Maher and Stevenson (1988) and Sleep et al. (1989) reinforced the idea that environments like that of the deep ocean hot springs are the favored environments for chemical evolution. According to this view, Charles Darwin's "warm little surface pond rich in organic stew" never existed. Instead, only chemical evolution taking place in the deep ocean was shielded from frequent asteroid impacts that repeatedly vaporized the upper levels of the ocean during the heavy bombardment of Earth. However, Towe (1991), argued that not all conditions that are beneficial for prebiotic chemistry exist near submarine hot springs. For example, cycles of wetting of drying of reactants may have been required.

How, then, can we reconcile beneficial surface conditions for evolution of cometary reactants, arriving first at the surface, with the view of some planetologist that a "warm little surface pond" is apparently ruled out by adverse impact bombardment of the surface. The answer is that the origin of life in Darwin's "warm little surface pond" is not ruled out by the impact history of Earth. Chemical evolution of cometary reactants could have occurred at the surface after the end of the heavy bombardment when the surface was relatively free of giant sterilizing impacts. Moreover, Maher and Stevenson (1988) concluded that life could have existed before the end of the heavy bombardment because they *assumed* a specific time was required to originate life. However, because the exact time required to originate life is unknown, it is not possible to conclude that chemical evolution occurred only in the deep ocean during the heavy bombardment period.

We will now show that chemical evolution could have occurred at the surface even during the heavy bombardment period. This was possible because the time between 10 km diameter comet impacts like those at the K/T boundary would *always* have been much shorter than the time between impacts big enough to sterilize surface interfaces and interfere with chemical evolution. Thus, life could have originated on the surface from prebiotic reactants supplied by small comets even during the early heavy bombardment period.

Oberbeck and Fogleman (1989b,1990) gave the time interval, in years, between formation of impact craters of size larger than D_{mn} in the time between 4.25 and 3.8 billion years ago on Earth as, in years:

$$T_w = S \times k \{ 1 + \exp (t-t_0/T) \}^{-1} \{ (1\text{km}/D_{\min})^{1.8} - (1\text{km}/D_{\max})^{1.8} \}^{-1} \quad (9)$$

where S is the surface area of Earth in km., k is cratering constant, t is time in Gyr ago, t_0 is 3.2 Gyr ago, $T = 70$ my. When D_{\min} in equation (9) is 840 km. We obtained the time T_w between impact of objects with kinetic energy of 10^{34} ergs which is sufficient energy to sterilize the Earth surface by boiling away the photic zone of the Ocean (Sleep et al., 1989). A 10 km comet would produce a crater 100 km in diameter. For such events, we obtain the time T_w between impacts of 10 km comets by substitution of $D_{\min} = 100$ km in equation (9). Division of one value of T_w by another, gives the result that the ratio in time between surface sterilizing impacts and impacts of 10 km objects is 53. Therefore, it is apparent that there would have been sufficient time throughout the first billion years of Earth's history for chemical evolution of prebiotic reactants supplied by 10 km comets at the Earth's surface during the much larger time intervals between giant asteroid and comet impacts that were large enough to sterilize the entire surface of Earth. Thus, chemical evolution of cometary reactants could have occurred in the favorable surface interfaces envisioned by Lahav et al. 1978, Chang, 1988, Lerman, 1986), and Oberbeck et al. (1990) where prebiotic reactants from comets were first present on Earth.

Figure five shows a schematic for our perception of the favorable surface environments for chemical evolution of amino acids supplied by cometary impact. The concentrations of amino acids shown in the different environments of figure five are those that result from impact of a 10 km comet that were computed earlier as adjusted for different depths of water. Concentration in clouds are from Oberbeck et al. (1990). It is conceivable that, during the early history of Earth, comets could have been as large as 100 km or perhaps larger. If so, the concentration of amino acid in each environment would have been three orders of magnitude higher than the respective values shown in figure (5). Since the concentration of reactants in the terrestrial environment is of first order importance for chemical evolution, we believe that clouds and shallow water environments would have been the most favorable environments for chemical evolution of cometary amino acids. Certainly they would have been sufficiently high to be favorable for polymerization during subsequent cycles of wetting and drying that would have occurred on clay substrates in these environments.

Discussion.

Our evaluation of the role of comets in chemical evolution must be limited to the study of the fate of cometary amino acids. The amino acid data of Zhao and Bada (1989) are very important but limited because it consists of one series of measurements of amino acid density at one stratigraphic section in Denmark. However, this data makes it possible to infer the concentration of amino acids in the sea after the impact and the concentration makes it possible to explore the fate of amino acids in the terrestrial environment and to assess the effectiveness of comets relative to classical sources of prebiotic reactants. Were it not for the fact that we could use comet composition data for Halley comet together with amino acid yields from shock tube experiments to compute sea water-amino acid composition with the values compatible with values that we deduced from amino acid column density, we would be far less confident than we are about the probable sea water concentration of amino acid after the impact of a 10 km diameter comet. These results permitted us to speculate about the role of comets in the origin of life and to outline some critical elements which should be considered. It would be presumptuous to believe that our understanding of the origin of life is much advanced by this exercise. Nevertheless, it has enabled us to think about the interactions between a source of one prebiotic reactant and the terrestrial environments so that we can begin to ask how to study the question of chemical evolution of prebiotic reactants in the primordial terrestrial environment.

We used the observed amino acid concentration in the Cretaceous-Tertiary sediments to infer the concentration of amino acid in sea water just after the Cretaceous-Tertiary cometary impact. Conditions associated with the Stevns Klint site have persuaded us that the amino acids in sea water were in equilibrium with amino acids absorbed on clay while they were present in sea water in concentrations near their initial concentrations. This implies that clay particles were the dominant sinks for the amino acids. This, in turn, has suggested that it is important to think about individual impacts instead of cumulative impacts over geologic time because the amino acids would have been absorbed from sea water very quickly after each impact. Apparently, clay in sea water absorbed amino acids from sea water in times less than those measured in decades because otherwise ultraviolet light would have quickly reduced the concentration to lower levels than required to give their observed density on clay particles present in K/T sediments. Moreover, it appears that the initial

concentration of amino acid in sea water after the K/T impact greatly exceeded the concentration that could have been ever been produced from corona discharge in the atmosphere and deposition in the ocean.

Our results suggests that sinks for prebiotic reactants must be considered carefully during assessments of the effectiveness of cometary reactants for chemical evolution . This approach is different from that taken by others. Chyba et al. (1990) state that assessment of the average production rate of organics from all comets at different times in geologic history is the key parameter needed for assessment of the importance of comets to the origin of life. They estimate the average production of organic material for comets of all sizes. This approach has little relevance for evaluating the role of comets in chemical evolution because the quantity of organic compounds from a range of comets of different sizes cannot be used to calculate the concentration of amino acids in the sea after any specific comet impact. For example, equation (8) may be used to show that the difference in time intervals between formation of comets of vastly different sizes greatly exceeds the short time intervals over which various sinks such as clay acted to reduce the sea water concentrations of amino acids supplied by them.

However, the average production rates of amino acids from comet impact are useful as a guide to the potential of cometary impact for chemical evolution within which the effects of individual cometary impacts must then be evaluated. In order to obtain an overview of the production rate throughout geologic history, we now obtain a rate of production for amino acids from cometary impacts during geologic history and compare it to the rate of production of amino acids from electric discharge. We begin by differentiating the total mass of comets impacting Earth which has been given by Chyba (1990) and the differentiation gives:

$$dM/dt \text{ (Kg/Gyr)} = \alpha(23)(3.79 \times 10^7)(.99) [1 + \tau^{-1} (2.3 \times 10^{-11}) e^{T/\tau}] [m_2^{.53} - m_1^{.53}] \quad (10)$$

where alpha is 0.1 for comets τ , in Gyr, is .144, T is time in Gyr measured backward from the present and the largest mass m_2 is taken as 1.5×10^{18} kgms. We obtain from this expression, the mass of amino acids as a function of time. We use a production rate for amino acids by averaging the value of 1.4×10^{-2} moles/ kgm of HCON obtained earlier for synthesis of amino acids in the vapor cloud of the K/T comet and the value of

3.8×10^{-2} moles/ kgm that we infer from the column density of AIB the ratio of amino acids in carbonaceous impactors, and the mass of the K/T impactor. We adopt the value of 0.86 as the fraction of comets that is made up of HCON. Expressing the production rate in terms of moles of amino acids per year from all comets and normalizing to square centimeters of the Earth's surface we obtain the production rate of amino acids from comets:

$$dM/dT \text{ (Moles/cm}^2\text{.yr)} = 1.68 \times 10^{-12} [1 + \tau^{-1} 2.3 \times 10^{-11} e^{T/\tau}] \quad (11)$$

We used this production rate to compute the production rate of amino acids from comets of all sizes during geologic history and show the results in figure six. The production rate for electric discharge in a CO₂ atmosphere using the corona discharge energy fluxes assumed by Stribling and Miller (1987) are shown in the figure. Finally the production from corona discharge using the energy fluxes indicated by Chyba and Sagan (1991) and the amino acid yield data of Stribling and Miller (1987) are shown also in figure six. It may be seen from this that the production of amino acids from comets is greater than the production rate for amino acids from corona discharge until 3.5 billion years ago, the age of the oldest fossils. These results, coupled with the approach outlined earlier, suggest that, throughout geologic history, amino acids of cometary origin, would have been more important to the origin of life than amino acids synthesized by corona discharge.

Conclusions:

Amino acids could have been synthesized as a result of cometary entry. The amount of amino acids in the sediments at the Stevns Klint K/T boundary sediments can be calculated from the amino acid yield from shock tube experiments performed by Barak and Bar-Nun (1975) using CHON reactants having carbon-oxygen ratios similar to those of comets and the total CHON mass expected in a comet the size of that required to form the K/T impact. The concentration of amino acids inferred to have been in the sea from synthesis during cometary entry is then calculated and used, together with experimental clay amino acid absorption data to predict the density of AIB amino acids on clay particles in the Stevns Klint sediments. Predictions are found to be in agreement with observed values. This suggests that clay particles in suspension in sea water were in equilibrium with amino acid solutions. Because the amino acid

concentration required to give the absorption density on K/T clays exceed, by an order of magnitude, the concentration that would have been produced as a result of ultraviolet degradation after only decades it is concluded that amino acids must have been absorbed by clay from sea water quickly after the K/T impact and ultraviolet light was not the dominant sink.

The inferred concentration of amino acids in sea water after impact of a 10 km diameter comet is 10^{-9} M, 10^{-7} M, and 10^{-5} M in the deep ocean, inland sea, and tide pools respectively. The initial concentration in cloud drops exceeds 10^{-3} M. Therefore, the preferred sites for chemical evolution of prebiotic reactants from comets are cloud drops and tide pools.

Chemical evolution of life at the surface of a bombarded Earth could have occurred even in the presence of periodic surface sterilizing giant impacts because the time between the surface sterilizing impacts would always have been about fifty times as great as the time between ten km diameter comets which supplied new prebiotic reactants. It is shown that the concentrations of amino acids supplied by small comets were much higher than the equilibrium concentration of amino acids that would have been produced in the primordial oceans from electric discharge in a CO_2 atmosphere and deposition in the ocean. Moreover, the density of amino acids produced from electric discharge and absorbed on clay particles would have been much less than that produced from comet impact. Because the amount of amino acids produced by comets always exceeded the amount produced by electric discharge in the time before the age of the oldest fossils, comets were probably more important for chemical evolution of amino acids than corona discharge. Comets were highly effective agent for chemical evolution of amino acids.

Figure Captions.

1. Total amino acid yield per gram of HCON reactants in various gases used in the shock tube experiments of Barack and Bar-Nun (1975) plotted against the calculated ratio of oxygen and carbon in the reactants. Shown also are the calculated uncertainties in the ratio of carbon and oxygen obtained from the error bars for carbon and oxygen given in Delsemme (1989).

2. Calculated change in the concentration of amino acid in the shallow sea after the K/T impact. Initial concentration of amino acids is that obtained from two independent estimates: 1. observed AIB sediment column densities and ratio of total amino acid to AIB in carbonaceous chondrites 2. amino acid yield from figure one C/O ratio =1.4. and minimum mass of K/T impactor. Concentrations after initial concentrations are calculated assuming that ultraviolet light was the dominant sink.

3. Calculated change in amino acids in the shallow K/T sea from corona discharge in a CO₂ atmosphere and deposition in the sea followed by degradation by ultraviolet light as for figure two. Note that concentrations are much lower for about 150 years in the case of corona discharge than for cometary impact.

4. Calculated range in uncertainty of clay surface area per molecule of AIB amino acid on smectite clay in the K/T sediments compared to observed clay surface area per molecule of AIB on K/T smectite clay. Note that the uncertainty in AIB concentration in the shallow sea is due to the uncertainty in depth of water at the Stevens Clint site and the uncertainty in clay-AIB absorption coefficient is due to our lack of an absorption coefficient for AIB. The observed clay surface area per molecule of AIB agrees with the zone of uncertainty marked by the crosshatched area so that the AIB in sea water could have been in equilibrium with AIB absorbed on the smectite clay from which we believe the amino acid was extracted.

5. Preferred sites for chemical evolution. After impact of a 10 km comet the concentration of amino acids would have been highest in cloud drops and tide pools. These are also the sites where clays and cycles of wetting and drying would have been possible. Although prebiotic reactants from corona discharge would also have been highest here, the concentrations would have been much lower than the concentration of amino acids from cometary impact.

6. Total production of amino acids from impact of comets (using production deduced from K/T amino acid sediment concentration/synthesis) and from corona discharge in CO₂ atmosphere (using energy flux of 12.5 Joule/cm². yr, Stribling and Miller, 1987 and 0.4 Joule/ cm². yr, Chyba and Sagan, 1991).

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AMINO ACID YIELD AS A FUNCTION OF O/C RATIO FOR BARAK AND BAR-NUN (1975) SHOCK TUBE EXPERIMENTS

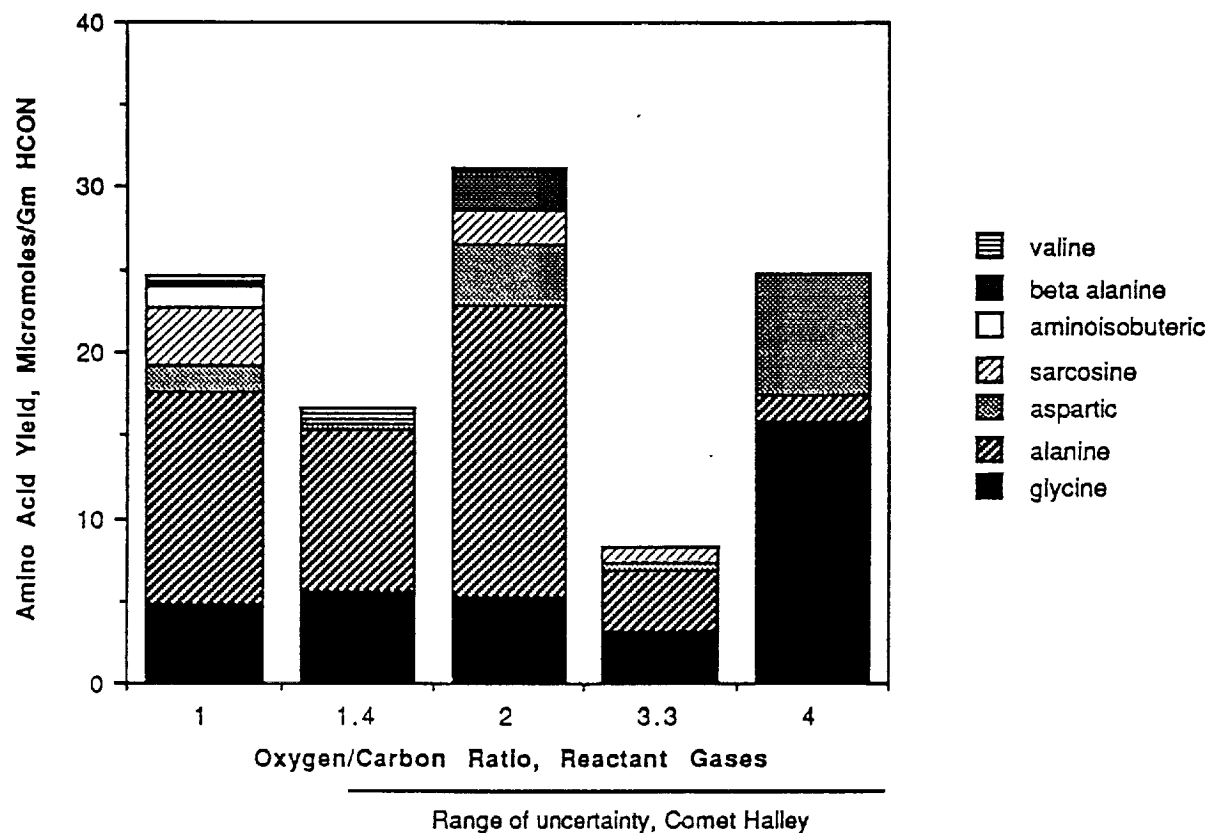


Fig 1

Amino Acid Concentration in 100 m Sea
from Amino Acids in K/T Sediments (UV Sink)

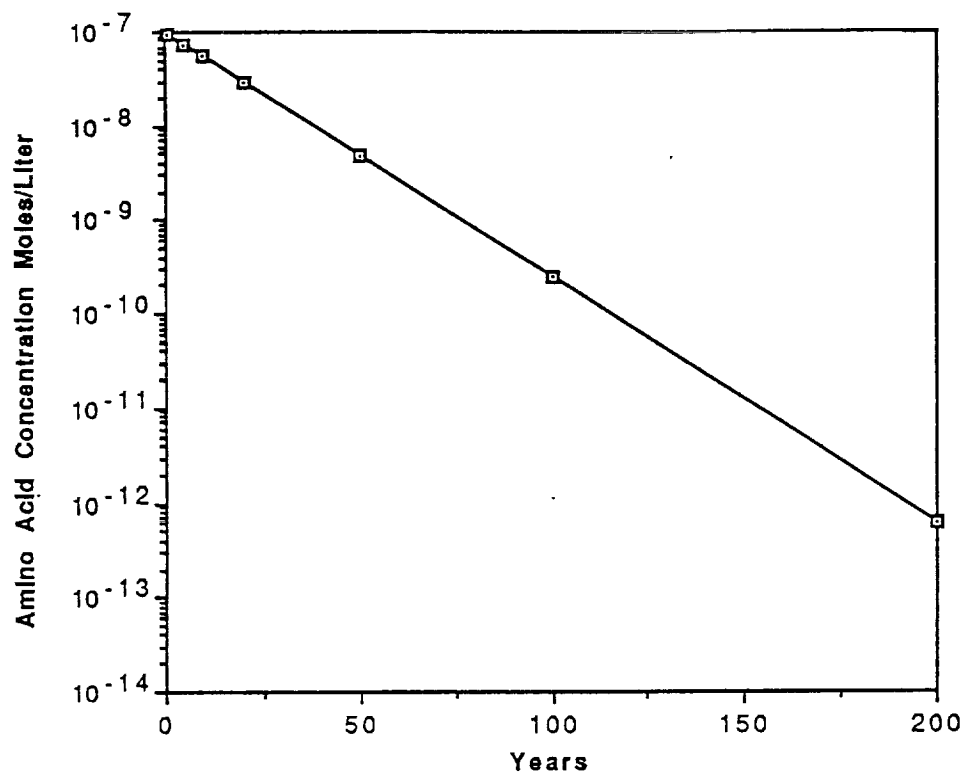


Fig 2

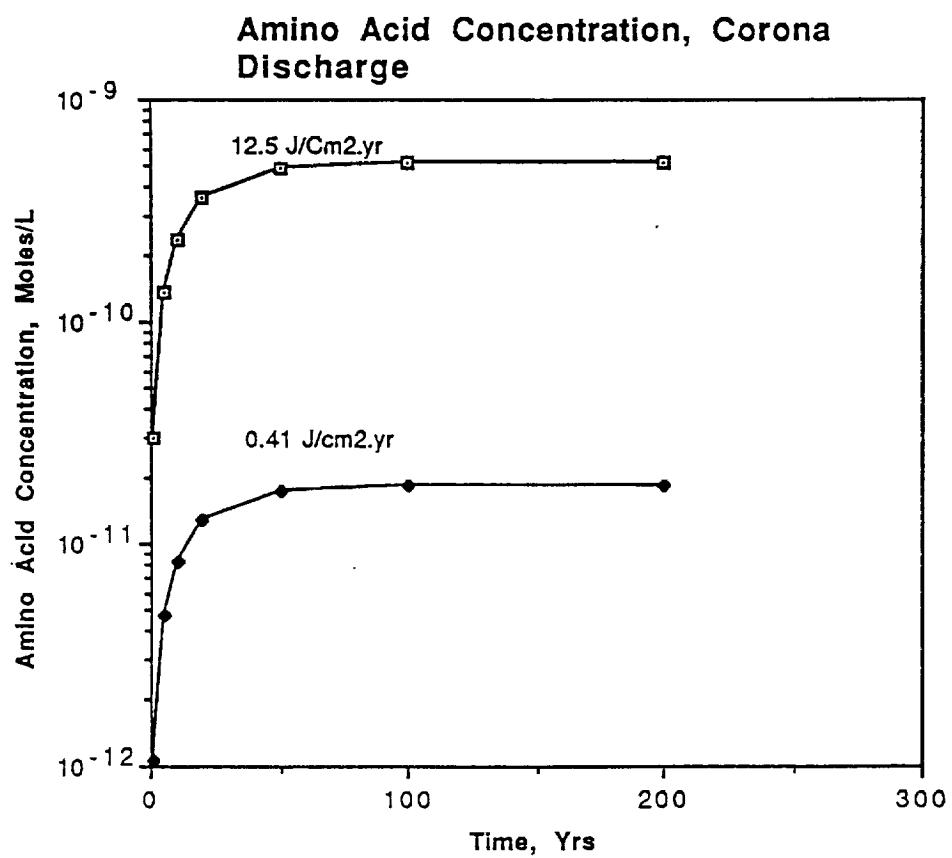


Fig 3

PREDICTED AND OBSERVED SURFACE DENSITY PER MOLECULE AIB FOR K/T EVENT

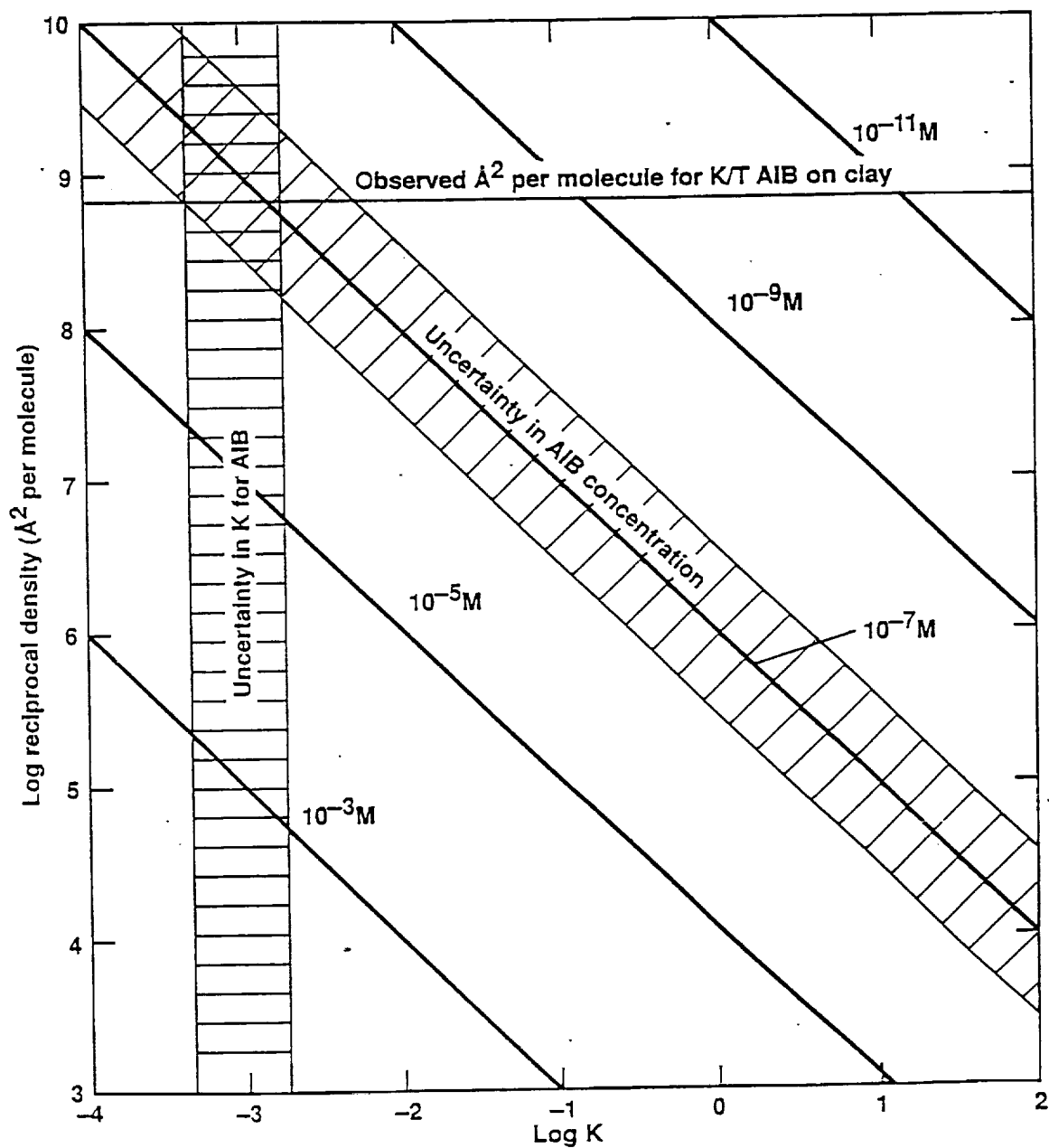


Fig 4

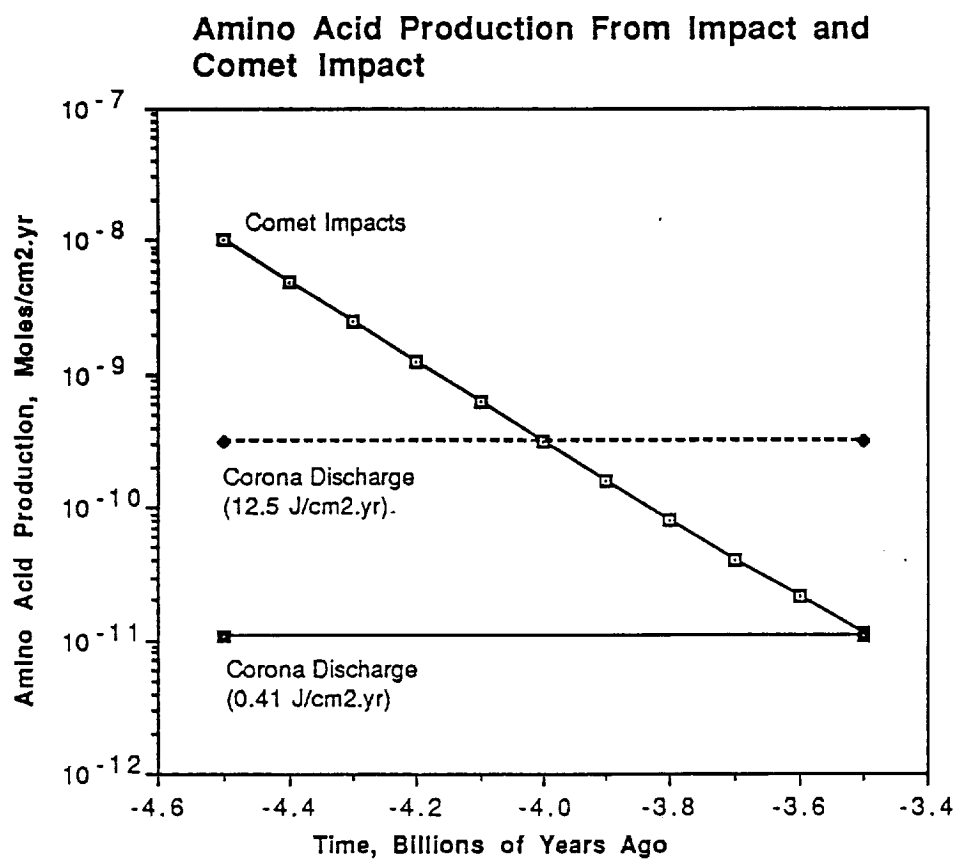


Fig 5

INFERRED FAVORABLE ENVIRONMENTS FOR CHEMICAL EVOLUTION

Conditions favorable for chemical evolution

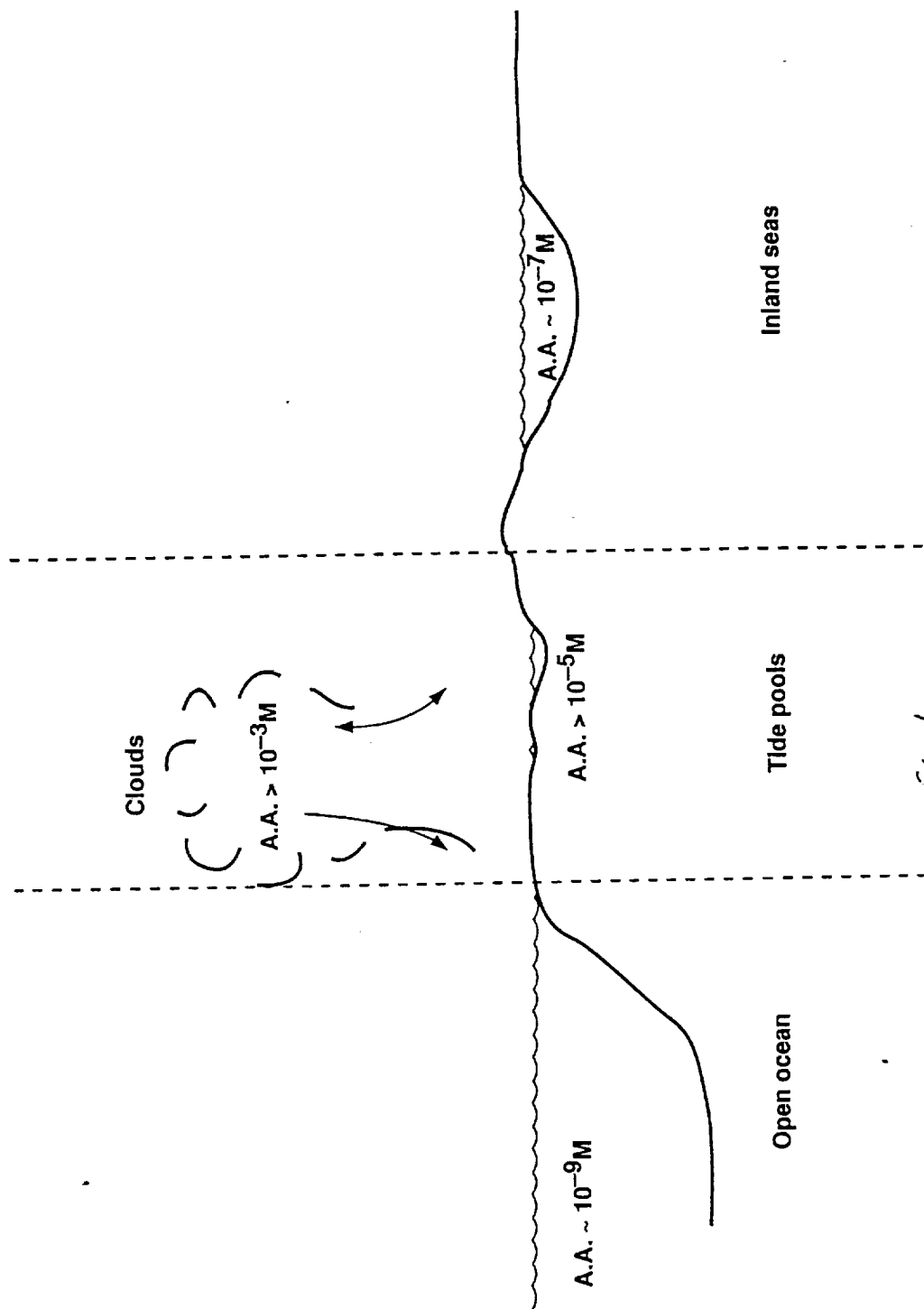


Fig 6